

Formation of Protective Silicide-Aluminide Coating on Gamma-TiAl Advanced Material

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Abstract—In this study, the Si-aluminide coating was prepared on gamma-TiAl [Ti-45Al-2Nb-2Mn-1B (at. %)] via liquid-phase slurry procedure. The high temperature oxidation resistance of this diffusion coating was evaluated at 1100 °C for 400 hours. The results of the isothermal oxidation showed that the formation of Si-aluminide coating can remarkably improve the high temperature oxidation of bare gamma-TiAl alloy. The identification of oxide scale microstructure showed that the formation of protective $\text{Al}_2\text{O}_3+\text{SiO}_2$ mixed oxide scale along with a continuous, compact and uniform layer of Ti_5Si_3 beneath the surface oxide scale can act as an oxygen diffusion barrier during the high temperature oxidation. The other possible mechanisms related to the formation of Si-aluminide coating and oxide scales were also discussed.

Keywords—Gamma-TiAl alloy, Si-aluminide coating, slurry procedure, high temperature oxidation.

I. INTRODUCTION

THE γ -TiAl based alloys are one of the most advanced materials that have drawn significant attention recently due to their interesting properties [1]-[3]. The attractive properties of γ -TiAl are low density (3.7-3.9 g/cm³), high strength and stiffness at elevated temperatures, good oxidation and creep resistance up to moderately high temperatures and high melting point [4]-[8]. In recent years, they have successfully proven their potential for aerospace and automotive applications, such as turbine blades, exhaust valves, and turbocharger rotors [9]-[11]. However, the oxidation resistance of this alloy is inadequate at elevated temperatures above 800 °C and thus has greatly limited its further applications [12], [13]. This is explained by the fact that γ -TiAl intermetallic compounds could not form a protective and dense Al_2O_3 layer, but form a brittle, porous and non-protective $\text{TiO}_2 + \text{Al}_2\text{O}_3$ mixed layer on their surfaces at oxidation environment in higher temperatures [14]-[18].

Various methods have been used to improve the oxidation resistance of γ -TiAl alloy at high temperatures. One of these approaches is the use of alloying technique [19]-[22]. This method is based on the suppression of TiO_2 formation that accounts for most of the mass gain of γ -TiAl during the high temperature oxidation. Park et al. [21] developed Ti-46Al-6Nb-0.5W-0.5Cr-0.3Si-0.1C alloy and found out that its oxidation resistance is superior mainly due to alloying elements such as Al, Nb, W and Si, which beneficially enhanced the formation of alumina and suppressed the formation of rutile in the scale. Yoshihara et al. [19] and Jiang

et al. [20] also used Nb as an alloying element and observed its beneficial effects on the improvement of oxidation resistance of the γ -TiAl alloy. However, the use of this method often leads to losing properties such as ductility at room temperature and creep resistance. Therefore, improving the oxidation resistance of γ -TiAl by using alloying elements for practical applications is not always beneficial [22].

Another approach to improve the high temperature oxidation resistance of γ -TiAl alloys is surface modification of them, which is known as the best method [23]. All coating methods can be placed in this category. Nishimoto et al. [24] prepared two-step Cr and Al diffusion coating on TiAl, Jung et al. [25] have prepared an Al+Y coating by a single EB-PVD process, Taniguchi et al. [26] also have deposited Thin Al_2O_3 layer by chemical vapor deposition (CVD) and a large number of other methods of coating for various other compounds have also been studied by various researchers for surface modification of TiAl alloy to improve its high temperature oxidation resistance [27]-[38].

Several researchers have prepared aluminide coatings on γ -TiAl alloy [38]-[41]. The Si-modified aluminide coatings are also prepared on γ -TiAl alloys by liquid-phase slurry method to form aluminide-silicide diffusion coatings on them [13], [30]. Based on thermodynamics, all titanium silicide phases (Ti_5Si_3 , Ti_5Si_4 , TiSi and TiSi_2) except Ti_3Si can form a protective SiO_2 layer on γ -TiAl alloy surface [42]-[44]. Owing to the good thermal stability, SiO_2 based coatings along with Al_2O_3 have been used to improve the high temperature oxidation resistance of γ -TiAl alloy [30].

The aim of the present work was to evaluate the high temperature oxidation of Si-aluminide coating on γ -TiAl and to investigate the relationship between the oxide scale microstructure and high temperature oxidation of γ -TiAl. The mechanism of oxidation resistance of protective oxide scale formed during isothermal oxidation was also discussed in this study.

II. EXPERIMENTAL PROCEDURE

In this project, γ -TiAl substrate with the chemical composition of Ti-45Al-2Nb-2Mn-1B (at. %) was used. The substrate was the coupons of size 10×10×2 mm³ which were cut from an ingot. The substrate surfaces were ground with SiC paper up to 1000 grit and then ultrasonically cleaned in ethanol and dried in air before the coating process.

The simultaneous aluminizing and siliconizing slurry process then were used to form the Si-modified aluminide coating onto the γ -TiAl substrate. This process was carried out

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by spraying the water-based slurry of Al-12wt.%Si (SermaLoy J) onto the γ -TiAl substrate. Then, the coated substrate was cured at an oven temperature of approximately 110 °C for at least 4 hours. The coated specimen was then placed into an alumina tube furnace. The furnace was circulated with Argon gas with purity of 99.99% and it was heated to 330 °C and held at this temperature for 3 hours until the binder transformed to a glassy solid and then the temperature was raised to a final temperature of 950° C at a heating rate of 10 Kmin⁻¹ and was held there for 8 hours. At the end of the coating period, the specimen was allowed to be cooled in the furnace to room temperature while maintaining the argon gas flow.

In order to evaluate the oxidation resistance of the coated specimen, isothermal oxidation test was done in static air at 1100 °C. The specimen was placed in a tube furnace oxidized at 1100 °C for 400 hours. The sample weights were measured to 0.0001 g only in the beginning and at the end of the oxidation process.

The XRD analysis was performed by ARL EQUINOX 1000. Also, the cross-section of the coating and oxide scale microstructures was analyzed by a ZEISS SIGMA VP field emission scanning electron microscope equipped with an Oxford energy-dispersive X-ray spectroscopy (EDS) detector and back scattered electron imaging facilities.

III. RESULTS AND DISCUSSION

A. Phase Identification and Microstructural Analysis of Si-Aluminide Coating

The SEM image of the formation of Si-aluminide coating on the γ -TiAl substrate via the liquid-phase slurry process is illustrated in Fig. 1 (a). The XRD result of the obtained coating is plotted in Fig. 1 (b). Additionally, in Table I, the EDS analysis at the marked points in Fig. 1 (a) is presented. On the basis of these results, it is found that the Si-aluminide coating with the approximate thickness of 50 μ m is well adherent to the substrate and has a triple-zone structure. On the other hand, it should be noted that no voids and micro-

cracks are observed within the coating.

TABLE I
THE EDS ANALYSIS OF THE POSITIONS MARKED IN FIG. 1 (A)

Position	Chemical composition (at. %)					Deduced phases
	Al	Si	Ti	Mn	Nb	
1	69.74	4.83	22.80	0.44	1.23	TiAl ₃
2	20.81	48.88	28.48	0.58	1.18	τ_2 -Ti ₇ Al ₅ Si ₁₂
3	69.25	5.28	22.46	0.51	1.33	TiAl ₃
4	22.74	36.83	41.32	0.53	1.27	Ti ₅ Si ₃
5	66.92	0.58	30.24	1.22	1.28	TiAl ₂

According to the EDS and XRD analyses, the structure of this coating is a triple one which includes an outer layer containing TiAl₃ matrix with very fine dispersed τ_2 -Ti₇Al₅Si₁₂ grains, a middle layer containing TiAl₃ matrix with very thin Ti₅Si₃ lamellas, and an inner layer of TiAl₂ with a low amount of Ti₅Si₃ lamellas.

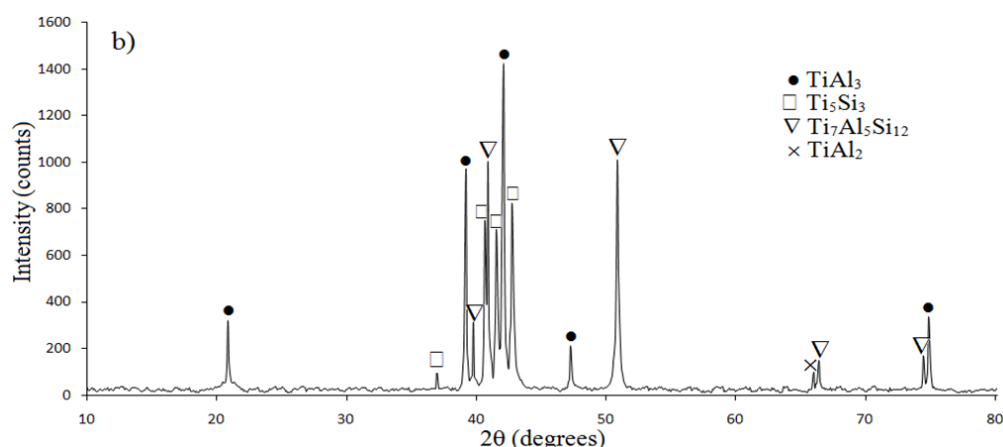
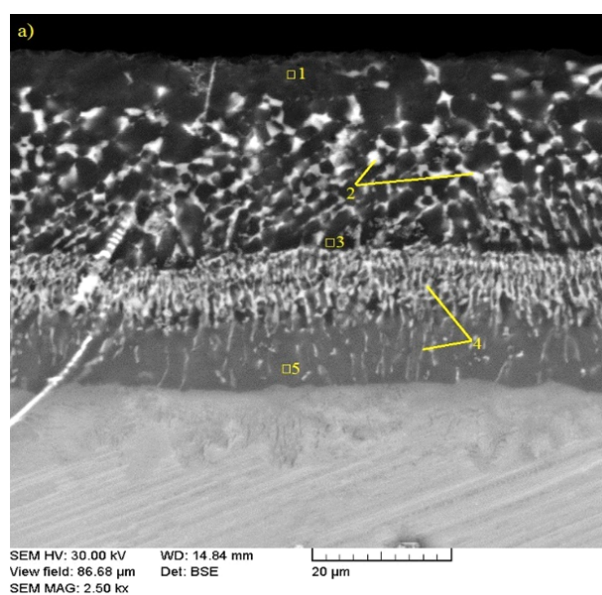


Fig. 1 (a) SEM cross-sectional micrograph of γ -TiAl coated specimen via slurry method and (b) XRD pattern of coated sample

In slurry coating procedure, during the diffusion treatment at 1000 °C, first, the powders of Al element available in the slurry were melted and then the powders of Si element available in the slurry was dissolved into the molten Al. Thus, different phases were formed within the coating by liquid phase diffusion of molten Al-12wt.%Si into the substrate. As a result of liquid phase diffusion into substrate, the Al available in the liquid reacted with titanium and formed TiAl_3 . Also, by diffusion of the liquid into substrate, Si present in the liquid reacted with the substrate's elements and formed the ternary compounds of $\tau_2\text{-Ti}_7\text{Al}_5\text{Si}_{12}$. Furthermore, binary compounds of titanium silicide (Ti_5Si_3) could be formed as the dominant products in different layers of the coating. Also, in accordance with the constant value of the thickness of the sample before and after coating process, it is concluded that the inward diffusion of Al and Si in the molten state is the dominant mechanism in the coating formation.

B. Oxidation Performance of the Si-Aluminide Coating

In Table II, the results of the isothermal oxidation test are presented at 1100 °C for 400 hours corresponding to the $\gamma\text{-TiAl}$ bare alloy and Si-aluminide coated sample. As can be seen in the results of the isothermal oxidation test, formation of Si-aluminide coating by liquid-phase slurry procedure significantly improved high temperature oxidation resistance of bare $\gamma\text{-TiAl}$ alloy. In fact, the mass gain of bare $\gamma\text{-TiAl}$ alloy is 221.3456 g/m² after 400h oxidation at 1100 °C, whereas, in Si-coated specimen, the mass gain dramatically reduces to 16.4625 g/m², indicating the improved oxidation resistance. Furthermore, there was a limited degree of spallation in Ti-45Al-2Nb-2Mn-1B (at. %) bare alloy, while spallation phenomenon was not observed in Si-coated specimen. The above-mentioned results represented that formation of Si-coating on $\gamma\text{-TiAl}$ alloy can greatly improve its high temperature oxidation resistance.

TABLE II
THE ISOTHERMAL OXIDATION TEST AT 1100°C FOR 400 H

Sample	Mass gain (g/m ²)	Spalled amount (g/m ²)
Bare $\gamma\text{-TiAl}$ alloy [Ti-45Al-2Nb-2Mn-1B (at. %)]	221.3456	56.3269
Ti-45Al-2Nb-2Mn-1B (at. %) alloy with Si-aluminide coating	16.4625	—

C. Phase Identification and Microstructural Analysis of the Oxide Scale

The SEM micrographs and the associated XRD results related to the formed oxide scales after isothermal oxidation at 1100 °C for 400 hours are illustrated in Figs. 2 and 3. Furthermore, in Table III, the EDS results of the marked points in Figs. 2 (a) and (b) are given.

In accordance with Figs. 2 (a) and 3 (a), it can be seen that the structure of oxide scales on the $\gamma\text{-TiAl}$ bare alloy is a porous two-layered one including an outer TiO_2 layer and an inner layer of mixed $\text{TiO}_2+\text{Al}_2\text{O}_3$. Also, some voids can be seen on the interface of TiO_2 and $\text{TiO}_2+\text{Al}_2\text{O}_3$ layers which are the essential factor in the spallation phenomenon occurred in the oxidized $\gamma\text{-TiAl}$ bare alloy.

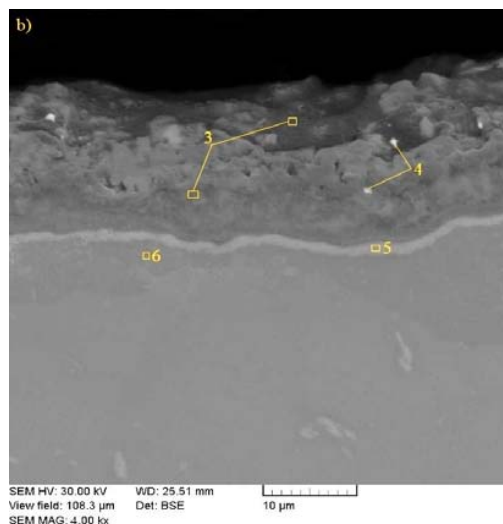
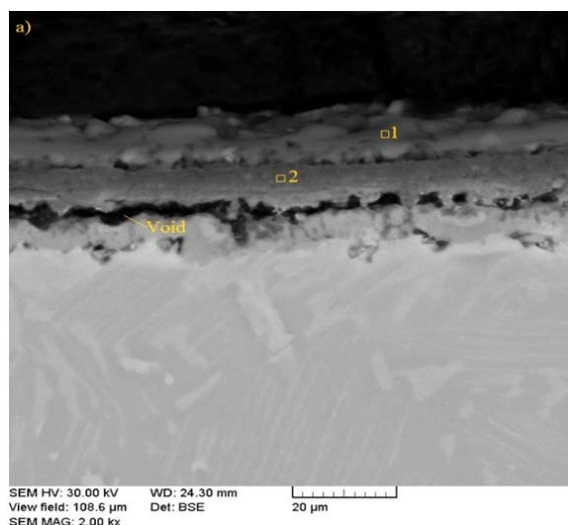


Fig. 2 Cross-sectional SEM images of $\gamma\text{-TiAl}$ alloys after isothermal oxidation at 1100°C for 400h, (a) bare alloy and (b) coated specimen

Based upon Figs. 2 (b) and 3 (b), it is demonstrated that the structure of oxide scales on the Si-aluminide coated sample via liquid-phase slurry process is a compact one without any void. This structure contains three separate zones including an outer protective oxide layer of $\text{Al}_2\text{O}_3+\text{SiO}_2$, a middle thin layer of $\text{Al}_2\text{O}_3+\text{Ti}_5\text{Si}_3$, and an inner layer of TiAl_2 together with Ti_5Si_3 lamellas. The absence of voids in the mentioned structure indicates that there is no spallation phenomenon during the oxidation procedure. It seems that the middle thin layer of $\text{Al}_2\text{O}_3+\text{Ti}_5\text{Si}_3$ acts as a barrier toward the oxygen diffusion to the substrate which causes to improve significantly the high temperature oxidation of the slurry

coated sample.

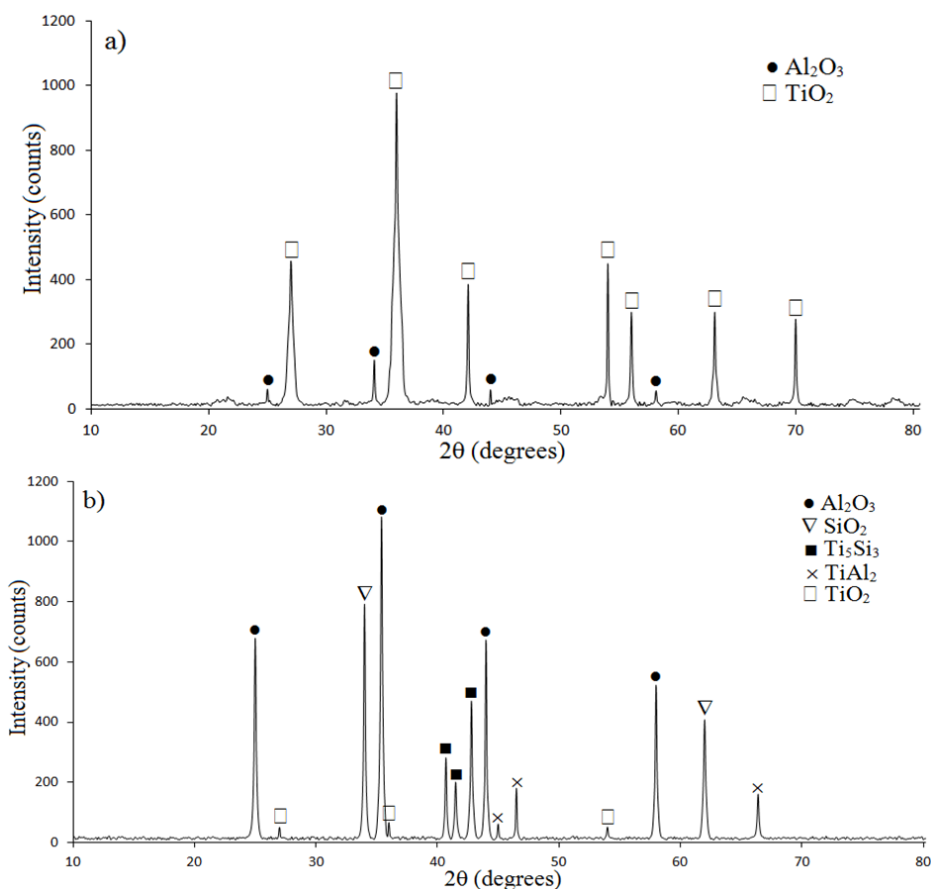


Fig. 3 XRD patterns of samples after isothermal oxidation at 1100°C for 400h, (a) bare alloy and (b) coated specimen

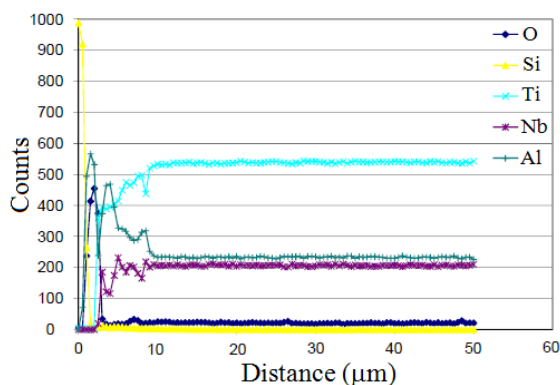


Fig. 4 Elemental line-scan profile of coated sample after isothermal oxidation at 1100°C for 400h

In Fig. 4, the elemental line scan profiles associated with the coated sample after isothermal oxidation at 1100 °C for 400h is demonstrated. In accordance with this figure, the absence of oxygen counts in beneath the protective $\text{Al}_2\text{O}_3 + \text{SiO}_2$ layer indicates that the Si-aluminide coating by liquid-phase slurry coating can act as a barrier to reduce the ingress of oxygen and improve the high temperature oxidation resistance of γ -TiAl alloy.

TABLE III
THE EDS ANALYSIS OF THE POSITIONS MARKED IN FIGS. 2 (A) AND (B)

Position	Chemical composition (at. %)				Deduced phases
	Ti	Al	O	Si	
1	24.81	—	75.19	—	TiO_2
2	16.90	14.21	68.89	—	$\text{TiO}_2 + \text{Al}_2\text{O}_3$
3	—	20.02	60.47	19.51	$\text{SiO}_2 + \text{Al}_2\text{O}_3$
4	42.33	17.02	—	40.65	Ti_5Si_3
5	52.67	8.88	14.80	23.65	$\text{Ti}_5\text{Si}_3 + \text{Al}_2\text{O}_3$
6	66.71	33.29	—	—	TiAl_2

IV. CONCLUSION

In present work, the Si-aluminide diffusion coating was prepared by liquid-phase slurry coating. The isothermal oxidation results at 1100 °C for 400 hours showed that the Si-aluminide coating can remarkably improve the high temperature oxidation resistance of γ -TiAl alloy. Based on the obtained results, it is demonstrated that the structure of oxide scales on the Si-aluminide coated sample via liquid-phase slurry process is a compact one without any void. This structure contains three separate zones including an outer protective oxide layer of $\text{Al}_2\text{O}_3 + \text{SiO}_2$, a middle thin layer of $\text{Al}_2\text{O}_3 + \text{Ti}_5\text{Si}_3$, and an inner layer of TiAl_2 together with Ti_5Si_3 lamellas. It seems that the middle thin layer of $\text{Al}_2\text{O}_3 +$

Ti₅Si₃ acts as a barrier toward the oxygen diffusion to the substrate which causes to improve significantly the high temperature oxidation of the slurry coated sample.

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